Rapid Communication

Magnetic phase transitions and magnetocaloric effect in the Fe-doped MnNiGe alloys*

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The magnetic phase transition and magnetocaloric effects in Fe-doped MnNiGe alloys are investigated. The substitution of Fe for Ni decreases the structural transition temperature remarkably, resulting in the magnetostructural transition occurring between antiferromagnetic and ferromagnetic states in $MnNi_{1-x}Fe_xGe$ alloy. Owing to the enhanced ferromagnetic coupling induced by the substitution of Fe, metamagnetic behaviour is also observed in TiNiSi-type phase of $MnNi_{1-x}Fe_xGe$ alloys at temperature below the structural transition temperature.

Keywords: magnetostructural transition, metamagnetic, magnetocaloric effect

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1. Introduction

Magnetic phase transition materials, which usually exhibit interesting physical properties, such as magnetocaloric effect, magnetoresistance and magnetic field-induced strain, have been extensively investigated in the past several decades because of their promising applications.[1−7] It is well known that the magnetic phase transitions can be classified into two categories: first-order phase transition (FOT) and second-order transition (SOT). Due to the large change of magnetization around the magnetic phase transition, the FOT materials have been extensively investigated. In order to obtain the optimized properties for application, many efforts, such as foreign atoms-doping,[8] structural and stress relaxation,[9] and introduction of elemental vacancy or interstitial atoms,[10−12] have been devoted to these materials to tune the phase transition.

Stoichiometric MnNiGe alloy shows a spiral antiferromagnetic (AFM) state below the Néel temperature (T_N) of 346 K. At about 470 K, it undergoes a crystallographic structural transition from the low-temperature orthorhombic phase (TiNiSi-type, space group $Pnma$) to the high-temperature hexagonal phase (Ni_2In-type, space group $P6_3/mmc$).[13,14] Since the structural transition takes place between two paramagnetic (PM) phases, it is difficult to identify them from the thermomagnetic curves. Early studies on the inverse susceptibility reveals a positive PM Curie temperature (θ_p, ∼277 K) in the hexagonal MnNiGe alloy, suggesting its ferromagnetism (FM) below θ_p.[13,15] Therefore, if the structural transition temperature (T_t) is greatly decreased to lower than the Curie temperature (T_C) of the Ni_2In-type phase, a magnetostructural transition occurring between AFM TiNiSi-type phase and FM Ni_2In-type phase can be obtained.[10] Moreover, the large magnetization difference between the AFM and FM phases would give rise to a large magnetic entropy change (ΔS_M). Recent studies reveal that the AFM/FM-type magnetostructural transition can be realized in artificially off-stoichiometric MnNiGe alloys by introducing vacancies of transition-metal atoms.[10,16] In this work, we investigate the effect of Fe-substitution in stoichiometric MnNiGe alloy and obtain the AFM/FM-type magnetostructural transition in low magnetic field due to the stability of the hexagonal phase regions. Accordingly, positive and negative values of ΔS_M can be observed around T_t and T_C, respectively.

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2. Experiment

Samples with a nominal composition of $MnNi_{1-x}Fe_xGe$ (x = 0.23, 0.24, 0.25, 0.26 and 0.27) were prepared by arc-melting the pure elements in argon atmosphere. After that, the as-cast ingots were annealed at 1173 K for three days in evacuated quartz tubes and were subsequently quenched in cool water. The crystallographic structures were investigated by X-ray diffraction (XRD) analysis using Cu-$K\alpha$ radiation at room temperature (RT). The magnetic measurements were carried out using a vibrating sample magnetometer (VSM, Lakeshore 7407) under a magnetic field up to 10 kOe (1 Oe = 79.5775 A/m).

3. Results and discussion

The powder XRD patterns for $MnNi_{1-x}Fe_xGe$ alloys at RT are shown in Fig. 1. It is known that stoichiometric MnNiGe alloy crystallizes in a TiNiSi-type structure at RT and transforms into the Ni_2In-type one at 470 K.[13] However, in the case of Fe-doped MnNiGe alloys, the Ni_2In-type instead of the TiNiSi-type structure is observed at RT, suggesting a remarkable reduction of T_t.

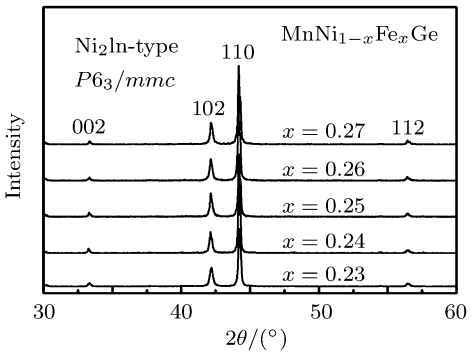


Fig. 1. XRD patterns for $MnNi_{1-x}Fe_xGe$ (x = 0.23, 0.24, 0.25, 0.26, and 0.27) alloys at RT.

Figure 2 shows the temperature dependence of magnetization (M–T) for $MnNi_{1-x}Fe_xGe$ alloys measured in a field of 1 kOe at temperatures ranging from 100 K to 300 K. On cooling, all the samples undergo the PM/FM phase transition around 216 K, suggesting the values of T_C are not sensitive to the composition. Further decreasing temperature results in rapid drops of magnetization, corresponding to the magnetostructural transitions from Ni_2In-type phase to TiNiSi-type phase, as previously observed in $(MnNi)_{1.9}Ge$ and $MnNi_{1-x}Co_xGe_{1.05}$ alloys.[10,16] The thermal hysteresis of about 8 K during the cooling and heating processes confirms the first-order nature of this magnetostructural transition. The value of T_t, defined as the temperature where $|dM/dT|$ is the maximum, decreases with the increase of Fe-concentration. Since MnFeGe alloy crystallizes in the Ni_2In-type structure in the whole temperature range,[17] the substitution of Fe for Ni would stabilize the Ni_2In-type phase reasonably, leading to the expanding of its temperature region, i.e., the decrease of T_t. On the other hand, the enhancement of the FM exchange interaction induced by the substitution of Fe would also contribute to the decrease of T_t to some extent. Moreover, the magnetization at temperatures below T_t increases with increasing Fe-concentration, suggesting the appearance of an induced FM ordering, which has been recently proved by the high-field magnetization study on $MnNi_{1-x}Fe_xGe$ alloys.[18]

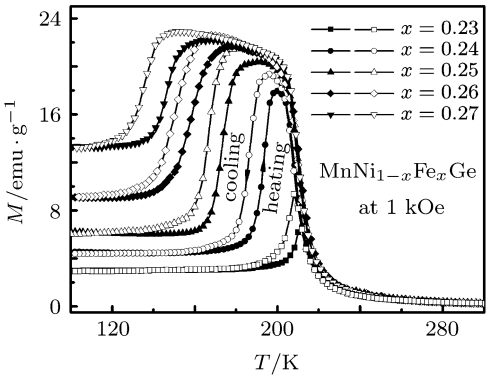


Fig. 2. Temperature dependence of magnetization curves for $MnNi_{1-x}Fe_xGe$ alloys on heating and cooling under the field of 1 kOe (1 emu = 10^{-3} A · m^2).

The isothermal magnetization (M–H) curves for $MnNi_{1-x}Fe_xGe$ alloys are measured at the temperature of 100 K, which corresponds to the TiNiSi-type phase, as shown in Fig. 3(a). The M–H curves show almost linear behaviour in low magnetic field, indicating the typical AFM character. However, in the magnetic field higher than 5 kOe, a series of metamagnetic transitions associated with small magnetic hysteresis between the field-up and field-down processes are observed, which has not been observed in the transition metal-vacant MnNiGe alloys.[10,16] It was reported that the Ni atoms in MnNiGe alloy is nonmagnetic, leaving the moments of Mn atoms aligning in the spiral AFM ordering.[19] In the case of MnFeGe alloy, the moments localize on both Mn and Fe sites, showing a ferromagnetic state.[17,20] It is assumed that the substitution of Fe for Ni may introduce an FM coupling in the TiNiSi-type phase of $MnNi_{1-x}FeGe$ alloy,

which is similar to the case of the Co-substituted MnNiGe alloy,[21] leading to the increase of magnetization in low magnetic field, as observed in Fig. 2. Therefore, the co-action of the external magnetic field and the introduced FM coupling would further destroy the AFM ordering, giving rise to the metamagnetic transition in the Fe-doped MnNiGe alloy at temperatures far below T_t.

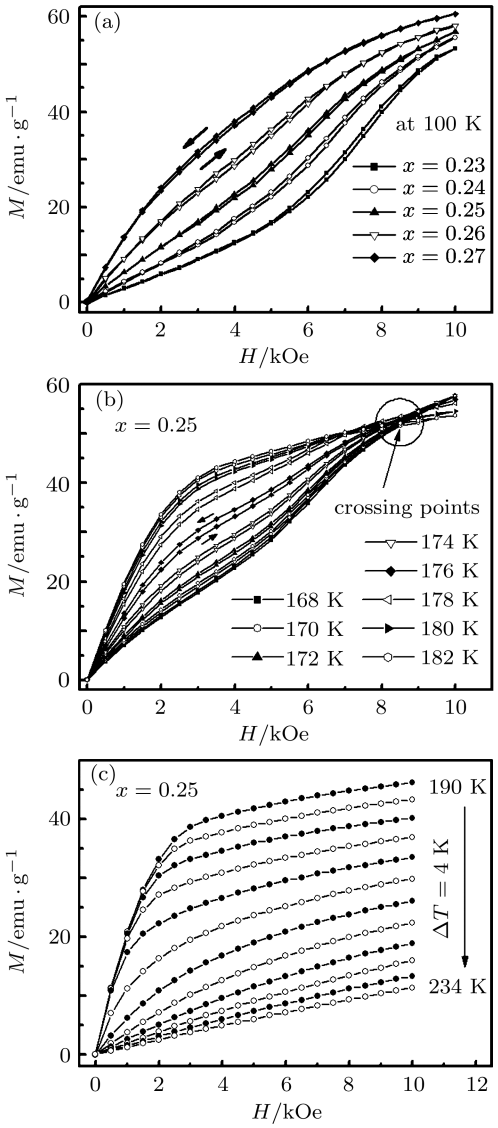


Fig. 3. (a) Isothermal magnetization curves for $MnNi_{1-x}Fe_xGe$ alloys at 100 K. Isothermal magnetization curves for $MnNi_{0.75}Fe_{0.25}Ge$ alloy around T_t (b) and T_C (c).

Figure 3(b) shows the M–H curves for $MnNi_{0.75}Fe_{0.25}Ge$ alloy measured around T_t. A series of metamagnetic curves corresponding to the magnetostructural transition between AFM TiNiSi-type phase and FM Ni_2In-type phase are observed, which is consistent with the results in Fig. 2. It is worth noting that, in the high magnetic field ($H > 8$ kOe), some crossing points appear in the M–H curves. As discussed above, the TiNiSi-type phase would also undergo a metamagnetic transition from AFM to FM under higher magnetic field. Therefore, at temperatures below T_t, for example 168 K, the FM TiNiSi-type phase and Ni_2In-type phase would coexist in the high magnetic field. At temperatures above T_t, for example 174 K, only FM Ni_2In-type phase exists. Since the magnetic moment in FM TiNiSi-type phase would be larger than that in FM Ni_2In-type phase,[12] some intersections are observed in the high magnetic field.

Figure 3(c) shows the isothermal M–H curves for $MnNi_{0.75}Fe_{0.25}Ge$ alloy measured around T_C. Typical FM and PM features are observed below and above T_C, respectively. No metamagnetic behaviour is found around T_C. The magnetization decreases gradually with increasing temperature, owing to the second-order of the FM/PM phase transition.

The ΔS_M as a function of temperature for each sample in a magnetic field change of 10 kOe is calculated from isothermal magnetization curves using the Maxwell relation, as shown in Fig. 4. Positive and

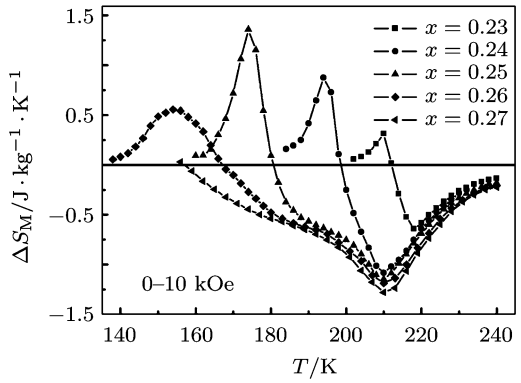


Fig. 4. Temperature dependence of magnetic entropy changes for $MnNi_{1-x}Fe_xGe$ alloys around T_t and T_C.

negative ΔS_M are exhibited around T_t and T_C, respectively. The peak values of ΔS_M of FOT and their related working temperatures change remarkably with the variation of Fe content. The second-order FM/PM phase transitions, which also result from the substitution of Fe, possess comparable peak values of $|\Delta S_M|$ with that in FOT. As we know, the refrigerant capacity, which is calculated by numerically integrating the area under the ΔS_M–T curves using the temperatures at half-maximum of the peak as the integration limits, is another important parameter to evaluate the magnetocaloric property. Compared with the small refrigerant capacity of 7.7 J/kg around T_t, a larger value of 33.4 J/kg is obtained around T_C in the low

field of 10 kOe for $MnNi_{0.74}Fe_{0.26}Ge$ alloy, suggesting that the second-order FM/PM phase transition is more suitable for magnetic refrigeration than the first-order ones in the present system.

4. Conclusions

The structural transition of MnNiGe alloy takes place between two paramagnetic phases. Appropriate substitution of Fe for Ni results in the occurrence of a first-order AFM/FM magnetostructural transition and a second-order FM/PM transition, owing to the remarkable decrease of magnetostructural transition temperature. Due to the introduced FM coupling in Fe-doped MnNiGe alloys, the TiNiSi-type phase also exhibits obvious metamagnetic behaviour at temperatures below T_t. The $MnNi_{1-x}Fe_xGe$ alloys show positive and negative ΔS_M around the FOT and SOT temperatures respectively, and the refrigerant capacity of SOT is larger than that of FOT.

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